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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

A Study of the Kinetics of Tin Electrodeposition from Sulfate **Electrolyte with Organic Additives**

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Abstract—The method of Faraday impedance was applied to study the kinetics of tin electrodeposition from a sulfate electrolyte in the simultaneous presence of syntanol DS-10, formalin (37% solution), and benzyl alcohol.

Previously, the kinetics of tin electrodeposition from a sulfate electrolyte in the presence of syntanol DS-10 has been studied [1]. Dull tin coatings have been obtained in this electrolyte. It has been shown that the kinetics of tin electrodeposition depends on the electrode potential and is gaverned by a heterogeneous and a homogeneous chemical reactions.

In [2], the electrodeposition of tin from a sulfate electrolyte in the presence of syntanol, formalin (37% solution), and benzyl alcohol was studied. It was shown that that, with these organic substances present simultaneously in an electrolyte subjected to stirring, shining coatings are formed at $i_c = 4 - 12 \text{ A dm}^{-2}$.

It was of interest to study the kinetics of tin electrodeposition in the presence of these organic substances. This was done, as in [1], using the Faraday impedance method. The differential capacitance was measured during electrolysis with an R-5021 ac bridge at frequencies in the range 200 Hz-20 kHz on an electrode made of tin-coated platinum wire ($S = 0.126 \text{ cm}^2$), placed at the center of a platinum-black-coated platinum cylinder. Electrochemical measurements were carried out using a P-5878 potentiostat in an electrolyte stirred with a magnetic stirrer.

A tin layer 10 µm thick was deposited onto the surface of the working electrode. The electrode surface was refreshed before making a measurement at each potential. The discrepancy between the results of measurements in different series did not exceed 5%. The potentials are given relative to a standard hydrogen electrode. The differential capacitances in electrolytes with organic additives are given with account of the roughness factor f. The procedure for determining f was described in [3].

The results obtained in measurements of the differential capacitance C at different electrode potentials

show that C decreases with increasing frequency and is constant in the range 30-50 kHz. It was assumed on the basis of this fact that the differential capacitance measured at these frequencies is the capacitance of the electrical double layer (EDL).

The measurements were done using a series equivalent circuit. The C_b and R_b values obtained with an ac bridge were recalculated to $C_{\rm s}$ and $R_{\rm s}$ values [4]. The equivalence of the circuit was verified using the procedure described in [5]. The electrode impedance components R_s and $1/\omega C_s$ were studied in relation to $\omega^{-1/2}$.

The results obtained in measuring the cathode current density and EDL capacitance as functions of the electrode potential demonstrate that organic additives inhibit tin electrodeposition (Fig. 1, curves 1 and 2). At potentials in the range -0.3...-0.4 V the EDL



Fig. 1. (1) Cathode current density i_c and (2) differential capacitance of the electrical double layer, C, at 30 kHz vs. the electrode potential *E*. Electrolyte composition $(g l^{-1})$: $SnSO_4$ 30, H_2SO_4 100, syntanol 2; formalin and benzyl alcohol 6 ml \tilde{l}^{-1} each; mechanical stirring.



Fig. 2. Electrode impedance components (1, 2; 5, 6) R_s and (3, 4; 7, 8) $1/\omega C_s$ vs. $\omega^{-1/2}$ at different electrode potentials. Potential (V): (1, 4) -0.3, (2, 3) -0.4, (5, 7) -0.6, and (6, 8) -0.7.

capacitance is 5.9–6.1 μ F cm⁻². At E < -0.54 V the EDL capacitance and the electrodeposition rate increase. The inhibition of the process in the electrolyte with organic substances is due to their adsorption and formation on the electrode surface of a dense adsorption layer, which starts to disintegrate at E < -0.4owing to desorption of molecules of the organic substances [6]. Dull coatings are obtained at potentials in the range -0.2...-0.6 V, and shining coatings, at -0.7...-0.83 V. With account of these data, the Faraday impedance was measured at potentials of -0.3, -0.4, -0.6, -0.7, and -0.8 V. The dependences of $R_{\rm s}$ and $1/\omega C_{\rm s}$ on $\omega^{-1/2}$ are presented in Figs. 2 and 3, curves 1 and 2, whence it can be seen that R_s at 200 Hz varies within the interval 1–10 Ω cm² at all the potentials studied. At -0.3, -0.4, and -0.6 V, $R_{\rm s}$ grows gradually with increasing frequency and passes through a maximum to reach a constant value after that at a frequency of 20 kHz (Fig. 2, curves 1, 2, and 5). At E = -0.8 V, R_s varies in the range 0.9– 1.2 Ω cm² with frequency increasing in the interval 200–3000 Hz; at higher frequencies R_s increases to 1.6 Ω cm² (Fig. 3, curve 1). Extrapolation of R_s values to higher frequencies yields the ?transition resistance R_t . At E equal to -0.3, -0.4, and -0.6 V, R_t is, respectively, 8.5, 4, and 3 Ω cm² (Fig. 2, curves 1,



Fig. 3. Electrode impedance components (1) R_s and (2) $1/\omega C_s$ and (3, 4) phase shift vs. $\omega^{-1/2}$ at different electrode potentials. Potential (V): (1, 2) -0.8; (3) -0.3 and -0.6; and (4) -0.4, -0.7, and -0.8.



Fig. 4. Equivalent electric circuits of the process of tin deposition from a sulfate electrolyte with organic additives at different potentials. R_e is the electrolyte resistance; C_d , capacitance of the electrical double layer; R_t , the transition resistance; and C_r and R_r , the capacitance and resistance of a heterogeneous chemical reaction. Potential (V): (a) -0.3, -0.4, and -0.8; (b) -0.7 and -0.8.

2, and 5). At a potential of -0.7 V, R_s passes through a maximum with increasing frequency and then tends to zero (Fig. 2, curve 6). The capacitive components of the impedance, $1/\omega C_s$, much exceed R_s . At a frequency of 200 Hz and potentials equal to -0.3, -0.4, -0.6, and -0.7 V, $1/\omega C_s$ varies in the interval $16-40 \ \Omega \text{ cm}^2$ (Fig. 2, curves 3, 4, 7, and 8). With increasing frequency, $1/\omega C_s$ decreases, passes through a maximum at a certain frequency, and then tends to zero. The only exception is the potential of -0.8 V at which the $1/\omega C_s - \omega^{-1/2}$ dependence shows a decrease from 4.2 to 2.5 $\Omega \text{ cm}^2$ after the maximum (Fig. 3, curve 2).

Analysis of the results of impedance measurements suggests that the impedance dependences correspond to equivalent electric circuits with in-series connection of the transition resistance R_t , capacitance C_t and resistance R_r of a heterogeneous chemical reaction at E = -0.3, -0.4, and -0.8 V (Fig. 4a); and to in-series connection of the capacitance C_r and resistance R_r of a heterogeneous chemical reaction at E = -0.7 and -0.8 V (Fig. 4b).

Thus, it may be concluded that the process kinetics is governed by a transition reaction and a heterogeneous chemical reaction in obtaining dull coatings,

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and by a heterogeneous chemical reaction in depositing shining coatings. The transition resistance at E = -0.3, -0.4, and -0.6 V is due to the hindered stage of discharge of tin ions. The heterogeneous chemical reaction is of varied nature, depending on the electrode potential.

At the potential of maximum adsorption, E = -0.3and -0.4 V) the heterogeneous chemical reaction is determined by the stage of tin ion penetration to the electrode surface across the adsorption layer. In this case, the process kinetics is governed by the so-called "penetration overvoltage" [7].

At E = -0.6 and -0.7 V, when the adsorption layer starts to disintegrate because of the desorption of organic substances from the electrode surface, the heterogeneous reaction is the chemical reaction of tin atoms adsorbed on the electrode surface with organic substances or products of their reduction. The heterogeneous chemical process occurring at E = -0.8 V is crystallization, with the transition resistance $R_t = R_{\rm cr}$ (crystallization resistance), $R_{\rm cr} = 2 \ \Omega \ {\rm cm}^2$.

As already noted, at E = -0.8 V the capacitive component of the impedance reaches a constant value after passing through a maximum. Extrapolation of $1/\omega C_s$ to higher frequencies yields a value $1/\omega C_{cr}$, where C_{cr} is the crystallization capacitance. According to the data of [5]

$$C_{\rm cr} = z^2 F^2 C_{\rm ad} / RT,$$

where C_{ad} is the concentration of adatoms on the electrode surface, z is the charge of tin cations, and F is the Faraday number.

The calculations performed demonstrate that $C_{ad} = 2.6 \times 10^{-14} \text{ mol cm}^{-2}$ for tin. The assumption that heterogeneous reactions occur depending on the electrode potential is also confirmed by measurements of the phase shift δ . The phase shift was calculated in accordance with [5]. With account of the ω_{max} value found from the dependence $1/\omega C_s - \omega^{-1/2}$, the reaction rate constant k was determined. For a heterogeneous reaction, $\omega_{max} = k$ and tan $\delta = -\omega/k$, $\delta \rightarrow -90^{\circ}$. The results of calculations are presented in Fig. 3, curves 3 and 4. It can be seen that the phase shift does approach -90° at potentials of -0.3...-0.8 V.

To conclude, it should be noted that the experimental data on the kinetics of tin electrodeposition from sulfate electrolytes with organic additives, obtained in [1] and in the present study, indicate that, in depositing dull coatings, the rate of the process is determined by a transition reaction and a heterogeneous and homogeneous chemical reactions. At the same time, when shining coatings are deposited, the kinetics of the electrodeposition process is determined by a heterogeneous chemical reaction, which has varied nature depending on the electrode potential.

CONCLUSIONS

(1) A study of the kinetics of tin electrodeposition from a sulfate electrolyte in the presence of syntanol DS-10, formalin (37% solution), and benzyl alcohol by the method of the Faraday impedance established that the kinetics of the process in the range of potentials at which dull tin coatings are formed is determined by a transition reaction and a heterogeneous chemical reaction.

(2) In the range of potentials at which shining coatings are formed, the process rate is determined by a heterogeneous chemical reaction.

(3) It was shown that the part of the transition reaction is played by the hindered reaction of discharge of tin ions, and the heterogeneous reaction has varied nature, depending on the electrode potential. At potentials of -0.3 and -0.4 V, when a dense adsorption layer is formed on the electrode surface, the hindered stage of the process is penetration of tin ions across the adsorption layer.

(4) At more electronegative potentials (E = -0.6, -0.7 V), when the adsorption layer starts to disintegrate as a result of desorption of organic substances from the electrode surface, the role of the heterogeneous reaction is played by the interaction of metal atoms adsorbed on the electrode surface with organic substances or products of their reduction, and at E = -0.8 V, by crystallization.

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